I Ibero-American Research Symposium:

Opening frontiers through new materials

International Meeting of Young Researchers

"Sharing discoveries is as crucial as making them"

-Albert Einstein-

UVasens group from University of Valladolid presents:

I Ibero-American Research Symposium

Casa del tratado de Tordesillas (Valladolid, Spain), November 7th, 2023

Join us in an incredible trip to discover more about the research being carried out by young researcher from University of Valladolid in cooperation with Ibero-American research organizations, in the field of advanced materials, a new area of modern science.

UVaSens

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Welcome to the First Ibero-American Symposium: Opening Frontiers Through New Materials.
This event represents a unique opportunity to explore the scientific advancements and intercultural connections that drive innovation in the world of research and technology.

The relationships among Ibero-American countries have proven to be a powerful engine for the advancement of science. Throughout history, scientific and technological cooperation has enabled the sharing of knowledge, resources, and talent, accelerating progress in a wide range of disciplines. This Symposium provides an ideal platform to strengthen these relationships, foster collaboration, and promote the exchange of ideas and experiences among researchers in our community.

At this event, the role of advanced materials in science and technology will be particularly highlighted. Research and development of advanced materials have revolutionized numerous areas, from electronics and nanotechnology to energy and medicine. Innovation in the creation and application of these materials has become a fundamental pillar for addressing global challenges in our time.

Throughout today, we will have the pleasure of hearing from prominent experts and scientists from the University of Valladolid, as well as various universities in Brazil, Colombia, Cuba, and Venezuela. They will share their pioneering research in the field of advanced materials and demonstrate how these contribute to the progress of our societies. Additionally, we will explore the cultural diversity that characterizes Ibero-America, emphasizing how this richness enriches scientific and technological research, providing a unique perspective.

In this context of Ibero-American relations, we cannot overlook the profound importance of the Treaty of Tordesillas Houses where we find ourselves. These historical places, where the division of lands between Spain and Portugal was agreed upon in 1494, represent a cultural legacy and a meeting point between our two nations. They are living testimonies of our shared history and a reminder of how cultural and geographical ties have influenced how we have explored and understood the world.

Furthermore, we must not forget the significance of the Brazil Chair in the cultural sphere. This chair, dedicated to the study of the culture, history, and arts of Brazil, has enriched our understanding of cultural diversity in Ibero-America. It has served as a beacon of knowledge and has promoted the understanding of the rich Brazilian cultural heritage in the context of our region, contributing to strengthening cultural ties and fostering greater academic and artistic exchange.

We hope that this conference will be a space for inspiration, knowledge exchange, and the creation of collaborative networks. The organizing committee invites you to actively participate in all sessions, present your own research, and, above all, establish connections that endure beyond this event.

As we progress through this exciting day, let us remember that together we can reach new frontiers of knowledge, and our Ibero-American relationships are a valuable asset on our journey to a brighter future.

Thank you for your transfer of knowledge with us!

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Carta del Tratatado de Tordesillas, 1494

"... el futuro del hombre y el de nuestro planeta se basan en el uso racional de los recursos hídricos y energéticos."

(Declaración de Tordesillas. 8 de mayo 2010)

El CTRI-UVa, creado el 9 de junio de 2009 por la Junta de Gobierno de la UVa, sucede en sus tareas al Instituto Interuniversitario de Iberoamérica y Portugal, sección UVa, que ha realizado su labor en la sede de las Casas del Tratado de Tordesillas desde 1994.

Tiene como objetivo dar soporte académico y científico a las interacciones con Iberomérica de la Unversidad de Valladolid, con base en la actividad de investigación y de formación de investigadores de sus miembros y equipos.

Asimismo, es objetivo del CTRI-UVa, la creación de valor añadido interdisciplinar y servir de puente académico con Iberoamérica, estimulando y canalizando iniciativas de la Comunidad Universitaria.

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PROGRAM:

UVaSens

9.30-10:00	**Registration**
10:00-10:30	**Opening**
10:30-11:00	Clara Pérez González " *enhanced impedimetric sensors for food industry"*
11:00-11:15	Luis Eduardo Alonso Pastor "*Nanocomposite polymeric foams from in-situ polymerization: Enhancing performance and bringing new funcionalities"*
11:15-11:30	Suset Barroso Solares *"Funcionalización y modificación de la morfología de fibras poliméricas electrohiladas para diferentes aplicaciones"*
11:30-12:15	**COFFE BREAK**
12:15-12:30	André Campos Machado *"Langmuir and Langmuir-Blodgett Films applied on the development of bioactive compounds and biosensors"*
12:30-12:45	Patricia Nájera Morales *"Influence of the Surface properties of floating monolayers on the electrochemical behavior of Langmuir-Blodgett films-based biosensors"*
12:45-13:00	Violeta Hurtado García *"Nanocomposite fiber analysis and their interactions with salts in aqueous solutions"*
13:00-13:15	Manuel Herrero Villar *"Dynamic chemistry for the formation of reversible bonds in cross-linked polymers"*
13:15-13:30	Aránzazu Redondo Hernangómez *"Poly (methyl methacrylate) foaming in scCO2 and water "*
13:30-13:45	Antonio Martín Pinillos *"optimización de sensores MIP basados en chitosan para le detección de compuestos fenólicos"*
13:45-15:15	**LUNCH**
15:15-15:45	Ana Paola Echevarría Vélez *"Clarificación y concentración de zumos de fruta mediante procesos con membranas a escala planta piloto"*
15:45-16:00	Mauricio Masaru de Souza Ribero *"Valorization of crustacean shell residues: fractionation of proteins by microwave-extraction and applications of the residual solid"*
16:00-16:15	Andrea Casas González *"Supercritical water valorization of chitin in a continuous reaction system: Chitin nano-particles"*
16:15-16:30	Jorge Torre Ordás "New insights on the molecular confinement and aging of nanocellular polymers"
16:30-16:45	Victoria Midori Katata *"Dye detection through Molecularly Imprinted Membrane (MIM) based sensor"*
16:45-17:00	Nataly Alejandra Castro Ferro *"Solubility of NO from combustion gases in amines solutions "*
	CLOSENING AND WINE

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Enhanced Impedimetric sensors for food industry

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Keywords: Electronic tongue; Biosensor; Impedimetric; Dairy industry; Nanoparticles

Abstract

In this work, an impedimetric bioelectronic tongue (bioET) consisting of an array of interdigitated microelectrode sensors was developed and applied to discriminate chemical components commonly found in milk samples. Few studies of impedimetric bioETs applied in the dairy industry can be found in the literature due to the complexity of characterizing milk matrices. Therefore, the development and exploration of multisensory systems incorporating various advanced materials such as nanomaterials combined with biological molecules represent a relatively new research field [1-2].

To enhance the sensitivity and selectivity of the sensor array, the sensors were modified with silver nanoparticles (AgNPs) for their electrochemical properties, high electrical conductivity, and ability to amplify bioelectrochemical signals. Moreover, enzymes including galactose oxidase (GaOx), glucose oxidase (GOx), beta-galactosidase (β-gal), urease (Ure), and lipase (Lip) were immobilized on the sensor's surface. Atomic force microscopy (AFM) was utilized tocharacterize the sensors surface. Silver nanoparticles exhibited a uniform arrangement across the entire surface, and after enzyme immobilization, a noticeable increase in surface roughness was observed, indicating the successful binding of the biological molecules.

Impedance analysis of standard milk-related solutions (glucose, galactose, lactose, urea, and triglycerides) demonstrated that sensors with a higher concentration of AgNPs in their structure exhibited increased sensitivity to milk components, as it evidenced the decrease in the impedance module. Sensors combining nanomaterials with enzymes showed improved differentiation capabilities for increasing concentrations of the enzyme's target molecules. For instance, a sensor modified with AgNPs and glucose oxidase displayed lower impedance compared to other sensors when testing glucose due to enhanced enzymatic activity facilitated by the silver nanoparticles.

Following the analysis of standard solutions, a chemometric analysis of their responses was conducted using principal component analysis (PCA). This analysis revealed that the bioET developed could effectively discriminate between standard solutions (glucose, galactose, lactose, urea, and triglycerides), grouping them into five clusters based on their nature, accounting for 79% of the variance in the original data through the first two components of the system.

Finally, an analysis of milk samples with varying nutritional characteristics, such as fat, lactose, and urea content, was carried out. The utilization of the bio-ETdemonstrated a direct relationship between the content of interest molecules and the response of the impedimetric sensors, primarily due to changes in the interaction between the sensor's surface and the milk matrix. As expected, higher fat concentrations led to increased impedance due to their interference in the electronic transfer process. Furthermore, it was confirmed that the developed biosensors exhibited specific responses to milk samples with higher sugar and protein contents, ensuring a high degree of cross-selectivity within the system.

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Nanocomposite polymeric foams from in-situ polymerization.

Enhancing performance and bringing new functionalities

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Keywords: Nanoparticle, polymer-grafted nanoparticle, in-situ polymerization, polystyrene, nanocomposite, polymeric foam, gas dissolution foaming

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Polymeric nanocomposites are advanced materials that combine polymers with nanoparticles, such as carbon nanotubes or clay nanoparticles. This nanoscale combination imparts exceptional properties to polymers, such as increased mechanical strength, stiffness, abrasion resistance, and gas barrier properties. Furthermore, the incorporation of nanoparticles allows for the modification of transport properties, such as electrical or thermal conductivity. These improvements are due to the large surface area and the high surface-to-volume ratio of the nanoparticles.[1] However, to fully realize the advantages of nanocomposites, it is crucial to achieve both a homogeneous dispersion and an effective interaction between the nanoparticles within the polymeric matrix. Hence, the preparation of composites by in-situ polymerization is advantageous over melt-based techniques.[2]

In addition to their applicability in conventional polymeric matrices, nanocomposites have also proven to be highly promising in the creation of advanced polymeric foams. The incorporation of nanoparticles into the structure of foams can have a significant impact on their properties, such as density, mechanical strength, and thermal conductivity.[3] This leads to foams that can serve in a wide range of applications, from thermal insulation materials to structural components in the aerospace industry.[4]

In this work, we studied the production of polystyrene (PS)/sepiolite nanocomposite foams. PS/sepiolite nanocomposites were prepared by in situ polymerization process, with the aim of improving the dispersion of sepiolite and its interaction with the polymer. The sepiolite was surface modified by grafting the vinyl silane group, enabling it to form bonds with styrene during an in-situ polymerization process. By dynamic shear rheology, the formation of a percolation network was determined. Finally, the obtaining of foams from these composites was initially explored. It was observed that anchoring of sepiolite to polystyrene is crucial for generating cellular structures. The foam with modified sepiolite exhibited the highest expansion ratio and cell nucleation density, with an expansion ratio up to 3.5 times higher and a cell nucleation density up to 1.85 times higher than that of the foam produced with the neat PS, while those of the unmodified sepiolite did not expand.

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Funcionalización y modificación de la morfología de fibras poliméricas electrohiladas para diferentes aplicaciones

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El electrospinning es una técnica que permite la formación de estructuras multiporosas llamadas fibras, que presentan una alta relación superficie/volumen y puede alcanzar funcionalidades fisicoquímicas específicamente definidas proporcionadas por su composición. Mediante la correcta selección de los materiales y los parámetros de fabricación es posible cubrir un espectro amplio de aplicaciones. En concreto, hay tres aplicaciones de gran interés que ejemplificaré desde mi experiencia. La primera, fibras obtenidas a partir de Polimetilmetacrilato (PMMA), fueron utilizadas en la separación de emulsiones estables de aceite-agua, alcanzando eficiencias de absorción de aceite de 90% (20 g/g).[1] Posteriormente, se mezcló PMMA con policaprolactona (PCL), permitiendo alcanzar una capacidad de absorción de aceite de 25 g/g en emulsiones estables agua-aceite con 80 v.% de aceite. [2] Además, ha sido posible desarrollar nuevas generaciones de fibras de PCL, combinándolo con sepiolitas o nanopartículas de cobre como cargas activas, y confiriéndolas de esa manera la capacidad de eliminar nitratos (23 mg/g en tan solo 15 min) y pesticidas (hasta 40 mg/g en pocas horas, siendo además reutilizables). Para aplicaciones biomédicas, hemos desarrollado fibras altamente porosas, alcanzada por primera vez mediante el proceso de espumado, con las que se consigue una liberación constante de ibuprofeno durante casi un día y medio.[3] Actualmente se lleva a cabo un estudio preliminar para su uso como administración de fármacos en seres vivos. Finalmente, con la combinación de PCL con Poly(3,4-Ethylenedioxythiophene): Poly(Styrene Sulfonate) (PEDOT:PSS), y la tecnología de espumado por disolución de gas, se obtuvieron sensores electroquímicamente activos cuya morfología, controlada por el proceso de espumado, controla su sensibilidad al catecol.

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Langmuir and Langmuir-Blodgett Films applied on the development of bioactive compounds and biosensors.

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Keywords: Langmuir films; Langmuir-Blodgett; Biosensors; Bioactive compounds; Thin films.

Abstract

Langmuir and Langmuir-Blodgett (LB) films is an important have been applied to study interfacial activity in a wide range of fields, the aim of this work is to be showing one application of each technic and its importance in tissue engineering and bioelectronic devices, respectively.[1] Langmuir Films can be applied to mimic membrane cells, due to the thickness of one molecule, it can reproduce the surficial environment of cell membranes. The importance of this approach is to understand and describe part of the action mechanism of some bioactivity compounds or medicines, this knowledge can be applied with organic synthesis to produce compounds more likely to penetrate specific types of molecules. In this work will be presenting how the changes of specific organic functions can modify the behavior of isovanillin, a compound found in different plant species [2], in models cell membranes of erythrocyte (health cell) and tumor cells.

Langmuir-Blodgett films also have an important role in producing bioelectronic devices, since the nanostructured monolayer can incorporate enzymes or bioactive compounds [3], the substrate utilized to immobilize the monolayer (LB), can be applied to act as a sensor with different technics i.e. UV-Vis [4]and Cyclic Voltammetry[5]. The intention of this work is to show how we could be able to stabilize Laccase, witch is an enzyme that catalizes phenolic compounds into its respective ketone[6] , and applying it in LB sensors.

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Influence of the surface properties of floating monolayers on the electrochemical behavior of Langmuir-Blodgett films-based biosensors

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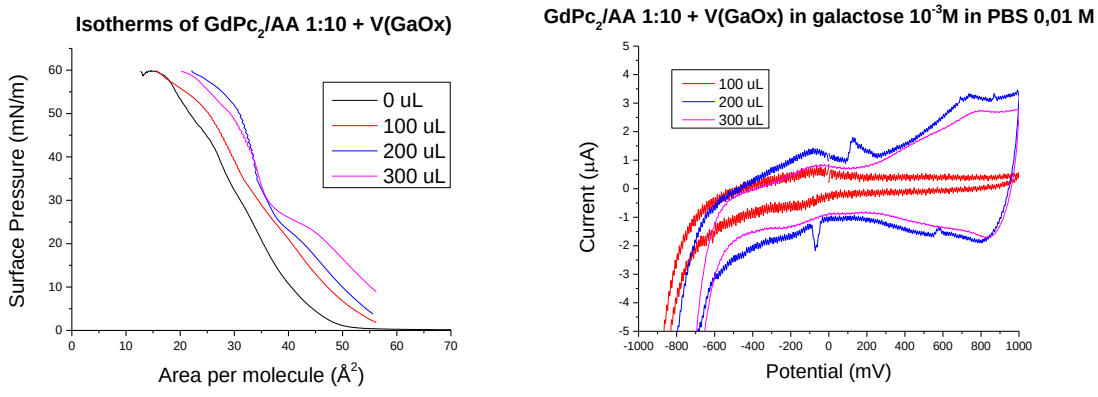
Keywords: Langmuir-Blodgett; phthalocyanine; galactose oxidase, isotherms, electrochemistry.

Abstract

The purpose of the present work was evaluating the correlation between the mechanical and rheological properties of different Langmuir matrixes and their subsequent electrochemical behavior as Langmuir-Blodgett films-based biosensors. To achieve that, we prepared three mixed systems based on different classic amphiphiles: arachidic acid (AA), dimethyldioctadecylammonium bromide (DODAB) and 1,2-dipalmitoyl-sn-glycero-3-phosphoglycerol (DPPG) **[1]**. All systems contained the electron mediator gadolinium bis-phthalocyanine ($GdPc_2$) to enhance the electrochemical response **[2]** and increasing amounts of the enzyme galactose oxidase (GaOx) due to study the detection of galactose as a common analyte in milk samples **[3]**.

The formation of Langmuir monolayers was carried out by spreading solutions of 1:10 $GdPc_2$/Amphiphile on the aqueous surface of a saline buffer and compressing in order to register surface pressure-area isotherms. Incorporation of increasing amounts of GaOx solution underneath the air-water interface was performed following a previous published procedure **[4]** confirming the penetration of the enzyme into the mixed monolayers by correlative increases of both the surface pressure and the area per molecule on the recorded isotherms in all cases. Brewster angle microscopy (BAM) images were taken. Rheological studies reveled the increasing fluidity of the films until saturation is achieved.



(**a**) (**b**)

Figure 1. Isotherms **a)** and cyclic voltammetry **b)** of the $GdPc_2$/AA/GaOx mixed system.

Langmuir monolayers were transferred to several substrates (ITO glass, quartz crystal and zinc selenide) by the Langmuir-Blodgett technique as established in the mentioned procedure **[4]**. LB films were characterized by UV-vis and Fourier transformation infrared (FT-IR) spectroscopies. Electrochemistry was carried out by cyclic voltammetry (CV) employing a standarized 10^{-3} M galactose solution in saline buffer. We found a correlation between the increasing area per molecule in the films due to the presence of the enzyme and the higher response of the transferred LBs. We intend to estimate the limits of detection, sensibility and the preservation of GaOx catalytic activity to evaluate the plausibility of transferred LB films to perform as specific biosensors.

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Nanocomposite fiber analysis and their interactions with salts in aqueous solutions

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Keywords: electrospun fibers; nitrates removal; sepiolite nanoparticles, AFM, mechanical properties

The high concentration of nitrates in aquifers, rivers, and open waters mainly due to the industrial use of fertilizers and livestock production is one of the main ecological problems facing society today [1]. In this work, nanocomposite fibers functionalized with different contents of modified sepiolite have been developed for nitrate adsorption. Their adsorption capacity (q) has been tested, reaching the value of q ~ 20 mg/g in an exposure time of 1 minute, as can be seen in Table 1. This is an improvement on materials dedicated to water decontamination in this field, which reach similar capacities but in contact times between 24 and 72 hours [2]. The nanocomposite fibers produced were foamed following the mehtod of gas dissolution foaming for fiber composites developed in [3] (named %SE-PCL-SPF mats). A multi-analytical characterization work has been carried out on both solid and foamed fibers by electron microscopy (SEM), thermogravimetry (TGA), differential scanning calorimetry (DSC) and atomic force microscopy (AFM). Furthermore, mechanical properties of the fibers in the AM-AFM mode have been tested both on solid and hollow fibers for different contents of sepiolite, the results of which are shown in Figure 1 (solid mats are named as %SE-PCL and hollow ones as %SE-PCL-SPF).

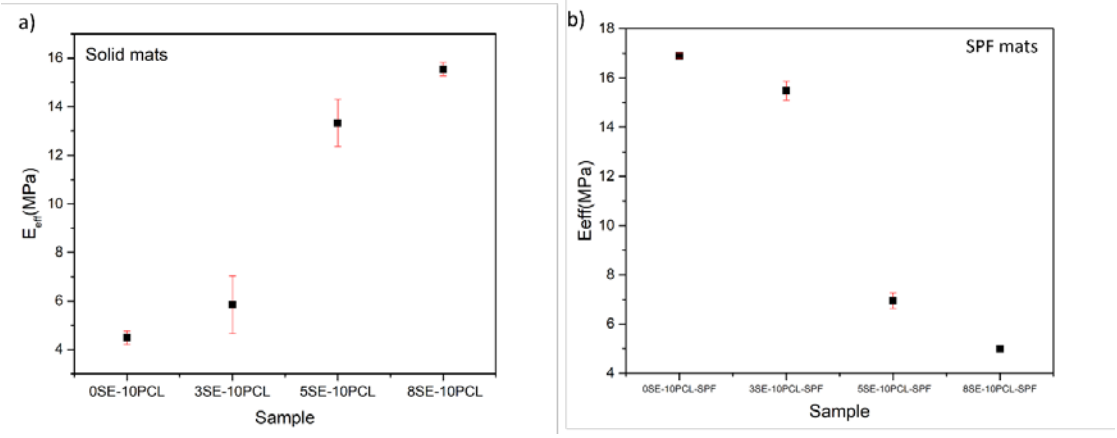

Figure 1. Effective Young's modulus of a) %SE-PCL fibers and b) %SE-PCL-SPF fibers.

Table 1. Absorption capabilities of the tested mats.

	5SE-10PCL			8SE-10PCL		
	1 min	15 min	30 min	1 min	15 min	30 min
Absorption capability (mg/g)	20.6 ± 8.6	20.0 ± 2.3	20.0 ± 3.9	20.8 ± 4.7	19.8 ± 1.4	19.8 ± 1.3

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Dynamic chemistry for the formation of reversible bonds in cross-linked polymers

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Keywords: Dynamic Chemistry; Vitrimers; Cross-linked polymers; Polymer Recycling.

Abstract

Vitrimers are a special type of polymer with the ability to rearrange their bonds in response to external stimuli such as temperature, light, or pressure [1-2]. The key feature is that these materials have dynamic or reversible covalent bonds that enable phenomena like shape changes or self-repair.

One unexplored field is their application in polymer foams. Traditionally, obtaining foams from thermoplastic materials requires a high degree of cross-linking. However, the formation of cross-linking points through irreversible covalent bonds greatly hinders the recyclability of these materials [3]. In this context, the current research is focused on creating highly cross-linked materials using dynamic covalent bonds. The bonds designed for Ethylene Vinyl Acetate (EVA) using boronic esters ensure the three-dimensional structure of the polymer, as well as its processability as a thermoplastic at high temperatures.

The tests carried out over the vitrimers showed small changes in thermal and mechanical properties with respect to the starting EVA. However, the rheological tests showed a high increase in viscosity, typical of cross-linked materials, which make these materials suitable for foaming processing.

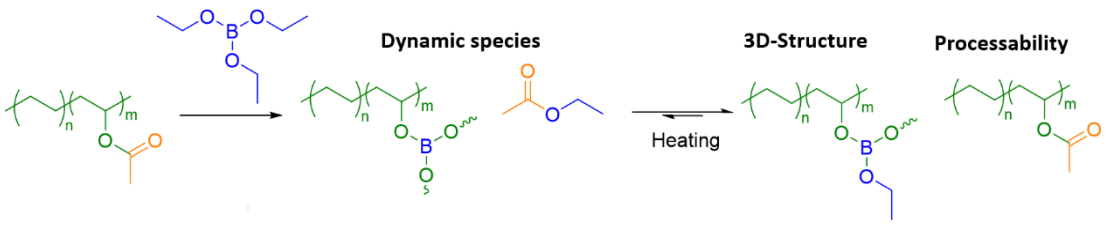

Figure 1. Functioning scheme of EVA vitrimer with the temperature.

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Poly (methyl methacrylate) foaming in scCO2 and water

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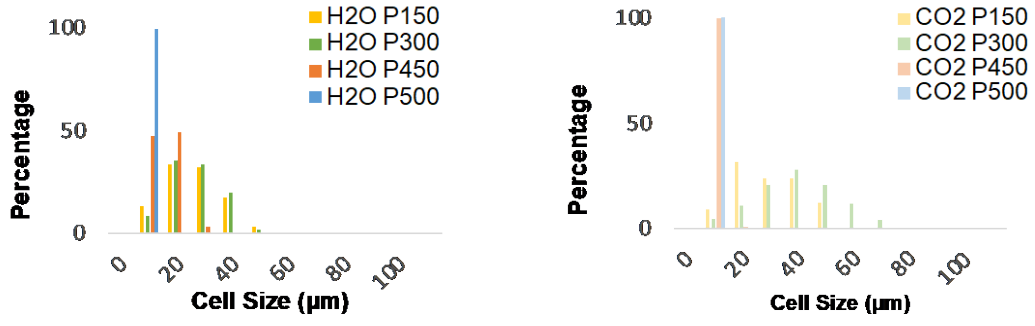
Keywords: PMMA, scCO2, water, foaming, polymers.

Abstract

Poly(methyl methacrylate) (PMMA) is a synthetic and amorphous polymer that belongs to the acrylate family. It presents high resistance to sunshine exposure, high impact strength, high scratch and shatter resistance, good degree of compatibility with human tissue, is a lightweight and exhibits favorable processing conditions and a reasonable resistance to chemicals [1]. Very promising application have been developed with PMMA in recent years through the polymer foaming with CO2. The produced foams present very low thermal conductivity, which make them a great insulation material [2]. This work study foaming of PMMA with supercritical CO2 in different conditions of pressure, time, temperature and particle size, to obtain nanoporous polymers. Also, recent research showed no PMMA modification under hydrothermal conditions [3], so the foaming process is carried out in the aqueous media to improve the cell number and reduce the cell size.

Foaming was carried out in High-Pressure foaming unit HPF-700. PMMA and water in different ratios were placed in a high-pressure tube autoclave and CO2 was also introduced in the system. The experiments were analyzed at different conditions such a pressure, particle size and time. The system was suddenly depressurized.

The foaming was achieved in all samples. The first results of the cell size distribution show similarities between the experiments with and without water, checking that this additive is working for foaming (Figure 1). Moreover, higher percentage of small cell sizes in the samples obtained in aqueous medium are obtained. Further experiments will be conducted to reach the best foaming conditions.



(**a**) (**b**)

Figure 1. Cell size distribution at different pressures: a) CO2 and aqueous medium; b) CO2

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Optimization of MIP sensors based on chitosan for the detection of phenolic compounds

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Keywords: molecular imprinted polymer; sensors; electrochemistry

Abstract

The need of the agroalimentary industry to determine the quantity of antioxidants present in food and drinks has led to the growth in interest in the use of sensors due to their excellent properties in the detection of phenolic or polyphenolic compounds. One of the many ways of preparing this sensors capables of providing selectivity, without need of introducing biological material, is based in the development of molecular imprinted polymers.

The synthesis of this molecular imprinted polymers is made through the polymerization of a reticulant compound, whose election is key to design the sensor, in presence of the interest molecule, to obtain a template of the analyte, which after its elution will serve for its later recognition. The polymer selected for the construction of this template is chitosan, this is due to their great capacity to form films through electrodeposition, and also capable of bearing the template molecule without deforming the design cavity.

This work is focus on the optimization of these "MIPs", electrodeposited in a chitosan film on glassy carbon electrodes. The electrodeposition is carried out using cyclic voltammetry in presence of the analyte (MIP) and in its absence (NIP). To optimize the results of these molecular imprinted polymers three parameters have been considered, time of exposition to vapours of glutaraldehyde, pH of the polymer solution and concentration of the template molecule, which in our case is catechol.

The results have been evaluated using cyclic voltammetry, looking for the difference of the intensity of the response between the NIP and the MIP, in order to confirm the advantages of this technique. Also, a quantity evaluation has been done to see the response of the synthesized sensors in different concentrations of catechol, showing an increase in the intensity of the redox peaks for the MIPs sensors.

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Clarificación y concentración de zumos de fruta mediante procesos con membranas a escala planta piloto

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Ke**ywords:** zumo de Frutas; ultrafiltración; osmosis inversa; enzimas; caracterización de Membrana.

Abstract

Los procesos de ultrafiltración (UF) se usan actualmente en la industria de zumos de frutas como alternativa a la clarificación convencional debido a su capacidad para llevarse a cabo a bajas temperaturas, lo que permite la conservación de compuestos sensibles al calor, tales como aromas y vitaminas. [1]. Asimismo, es posible utilizar la ósmosis inversa (OI) como etapa de concentración de zumos, pudiendo obtener un zumo concentrado de mejor calidad. [2]. La concentración de zumos de fruta, permite reducir el embalaje, el almacenamiento y los costes de transporte debido a la extracción de agua en el proceso final [3].

El objetivo de este trabajo fue evaluar el uso de ultrafiltración y ósmosis inversa para la obtención de zumos de fruta (melocotón, pera y manzana) clarificados y concentrados a escala planta piloto. Los zumos fueron tratados inicialmente con enzimas pectinolíticas a 50 ^{o}C durante 1 hora. Para el proceso de ultra filtración (UF) se utilizó una membrana tubular de polisulfona (8kDa) y 0.01µm de tamaño de poro, a una presión transmembranal de 0,5 MPa a 50 ^{o}C. (Figura 1). Finalmente, los zumos se concentraron por ósmosis inversa (OI) con membranas tubulares compuestas de una película de poliamida (99% de rechazo de NaCl) con una superficie de filtración de 0,9 m , trabajando con presiones transmembrana de 2 y 4 MPa, a 25-27 ^{o}C. Los parámetros analizados fueron: el flujo de permeado, sólidos solubles, viscosidad, densidad, pH, acidez, contenido de pulpa, color y presencia de pectina. El zumo clarificado de melocotón de 12,2 ^{o}Brix se concentró hasta 30,5 y 21,52 ^{o}Brix para 4 y 2 MPa de presión transmembranal, respectivamente. (Tabla 1) Las membranas utilizadas fueron caracterizadas físicamente mediante microscopía electrónica de barrido (SEM). [4].(Figura 2).

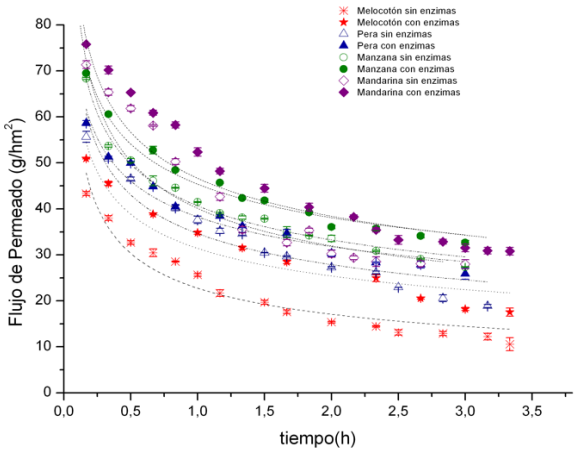

Figure 1. Flujo de permeado de los zumos de fruta con y sin enzimas en función del tiempo

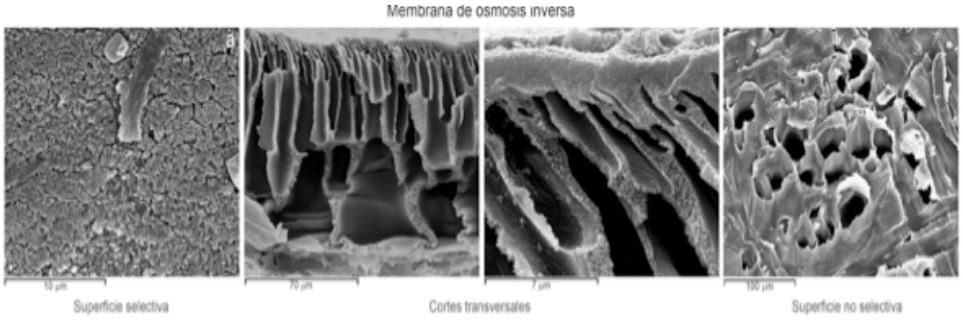

Figure 2. Membrana compuesta formada por dos capas: Capa selectiva: relativamente densa y delgada de un espesor medio de 1.1±0.4 µm. Soporte polimérico con un espesor de 99.5±4.2 µm

Table 1. Propiedades fisico-quimicas de los zumos (Inicial, UF)

Zumo		**S.S (ºBrix)**	**η (m.Pa.s)**	**ϱ (kg/m³)**	**pH**	**Acidez (g de acido citrico /100ml)**	**Pectina**
Melocotón	**Crudo**	12.1	1.04	1.062	3.77	0.63	(+)
	Sin enzimas	12.2	1.02	1.032	3.80	0.69	(-)
	Con enzimas	10.9	0.98	1.032	3.61	0.67	(-)
Pera	**Crudo**	11. 8	1.24	1.062	3.71	0.38	(+)
	Sin enzimas	12.0	1.04	1.053	4.09	0.40	(-)
	Con enzimas	11.9	1.02	1.050	4.08	0.41	(-)
Manzana	**Crudo**	12.2	1.63	1.038	3.71	0.38	(+)
	Sin enzimas	12.1	0.96	1.038	4.09	0.26	(-)
	Con enzimas	11.8	0.85	1.013	4.08	0.34	(-)

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Valorization of crustacean shell residues: fractionation of proteins by microwave-extraction and applications of the residual solid

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Keywords: Biorefinary; Shrimp shell; Protein; Calcium carbonate; Chitin

Abstract

The fishing and food industry generates large amounts of crustacean shells as waste from their processes. These shells contain 20-30% of chitin, 30-50% of minerals (mainly calcium carbonate - $CaCO_3$), 30-40% of proteins and other compounds in smaller amounts, such as lipids and pigments [1–3]. Chitin and its derivative, chitosan, are highly demanded products due to their interesting applications. Global valorization of crustacean shells may include protein recovery and development of applications for minerals. In the conventional process for the separation of chitin and its subsequent purification from the crustacean shells, three chemical processes are necessary: deproteinization, demineralization and decolorization, and chemical reagents potentially harmful to the environment are used for each of these steps [1,3]. To avoid the drawbacks realated to chemicals, development of greener and more efficient processes are under development for the valorization of this waste biomass [1,2].

In this context, this project aims to develop a biorefining process for the valorization of shrimp molting shells, by sequential fractionation with non-conventional techniques to obtain two differenciated products: 1) a protein concentrate and 2) a chitin-calcium carbonate composite that will be used as platform material for catalyst development and films production.

Initial composition of the raw material, *Litopenaeus vannamei* shrimp moult shell, is 53.7 ± 0.5% (g/100 g of dried shell) of ash (mineral), 3.8 ± 0.9% of fatty acid, 17.8 ± 0.7% of chitin (crude fiber), 10.6 ± 0.4% of protein, and 1.37 ± 0.12% of amino acids. The finded

chemical distribution in the shell agrees with the literature, where the molt shell has a higher mineral content compared to the amount in shells of adults animals of the same species [4].

Under optimized conditions (T: 210 °C, t: 6 min, S/F: 60 mL/g), 90% of the initial amount of proteins and amino acids have being recovered by microwave-assisted extraction using only water as solvent [5]. The residual solid from this aqueous extraction supposes a 60% of the initial solid mass, and is being characterized by elemental analysis, XRD, FTIR, and SEM. This solid will be studied for industrial application as a catalytic support [6,7] and for the production of biofilms [8,9].

Acknowledgements

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Supercritical water valorization of chitin in a continuous reaction system: Chitin nano-particles.

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Keywords: Chitin nano-particles, ultra-fast reactors, SCW hydrolysis.

Abstract

Chitin is an abundant biopolymer of [β-1,4-poly(n-acetyl-D-glucosamine)] units, produced by crustaceans, mollusks, insects, and fungi. Nowadays, chitin is discarded in massive amounts (6–8 million tons/year) as waste from the seafood industry, being underexploited as biomass resource[1]. Chitin is of great interest as a biocompatible and biodegradable material, gaining importance in the formulation of phytosanitary products, thanks to its elicitor activity in plants[2]. It is also considered as a source of oligosaccharides and biologically active monomers, N-acetylglucosamine (depolymerization) and glucosamine (deacetylation). Several studies have shown that chitin, like cellulose, can be dissolved and hydrolyzed in supercritical water (SCW) due to the change in its properties (water density and ionic product, among others); however, due to the high chitin crystallinity, this process occurs less easily[3].

The present work aims to investigate the mechanisms of chitin transformation in SCW medium (400°C and 25MPa), using ultrafast sudden expansion microreactors (SEMR) in a continuous system (residence time 0.1s - 2s). Special attention was paid to the effect of residence time on the depolymerization processes. Commercial chitin was used as raw material and characterized by elemental analysis (EA), FT-IR, Particle Size Distribution (PSD), zeta potential (ZP) and XRD. Total Organic Carbon, Total Nitrogen, pH and HPLC were used to characterize the liquid product; and solid fraction was characterized by EA, FT-IR, PSD, ZP and XRD for comparison with raw material. The results show that, within the studied conditions, chitin could not be fully depolymerized in SCW, at the highest residence time tested, the solid fraction was still 40%. Higher residence time caused partial solubilization and particle size reduction of the solid fraction. At lower residence time, particles with an average size of 582µm and a ZP of +32mV were obtained. These particles are being used in a proof of concept for the preparation of Pickering emulsions with phytosanitary purposes.

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Acknowledgements

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New insights on the molecular confinement and aging of nanocellular polymers

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Keywords: nanoporous; glass transition temperature; chain inmovilization; ATR; Raman.

Abstract

Nanocellular polymers are porous structures characterized by pore sizes in the nanometric range [1]. Reducing sizes in the geometry present in the cellular structure of nanocellular polymers is known to induce a molecular confinement in the polymeric matrix, which leads to properties such as higher resistance and stiffness or higher glass transition temperature (T_g) [2].

Our previous work [3] demonstrated the presence of this confinement in the solid phase of nanoporous PMMA-based materials, produced by gas dissolution foaming. As this was the first demonstration on self-standing three-dimensional nanoporous polymeric materials, more insights on the topic are needed. Therefore, the objective of this research is to further study this confinement effect at molecular scale using characterization techniques such as ATR and Raman spectroscopy, and DSC.

The results demonstrate the existence of a molecular confinement which affects mobility and vibrational behavior of polymeric chains. A study on the relaxation mechanisms revealed residual stresses after the fabrication, but the results obtained from thermally annealed samples and samples that have rested for 10 years indicated that the observed effects cannot be attributed to fabrication stresses. This establishes that the observed reductions in mobility are solely attributed to the phenomenon of molecular confinement in nanoporous polymer materials.

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Dye detection through Molecularly Imprinted Membrane (MIM) based sensor

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Abstract

Molecular Imprinting Technology (MIT) concerns the formation of selective sites of a molecule in a matrix, thus forming a memory of a template of the target molecule. Molecularly Imprinted Membranes (MIM) is one of the techniques used to obtain these templates. This alternative was developed for separation membranes, such as filtration [1]. However, these MIMs can also be used to manufacture sensors to detect emerging pollutants, for example. Methylene blue is a dye used in paper, silk, cotton, and hair dye and can cause adverse effects on human health, such as eye, mental disorders, and respiratory problems [2]. Therefore, methods for detecting MB are important. This work aims to create a selective electrochemical sensor for detecting methylene blue using MIM by deposition via Langmuir-Schaefer (LS). The phospholipid chosen as a membrane was DPPC. This membrane was deposited via LS, which refers to transferring Langmuir films to solid substrates through horizontal contact of the substrate surface on the monolayer. Deposition occurred with the DPPC membrane and DPPC in the presence of MB in the aqueous subphase ($1x10^{-4}$ mol/L), and the solid substrate used was ITO. The dye was removed from the film, leaving it immersed for 4 minutes in Milli-Q water so its template remained. The films were then characterized via cyclic voltammetry and UV-Vis, which effectively demonstrated the presence of MB in the film with the DPPC membrane. After washing, the results showed the dye removal from the substrate film. Therefore, MB was successfully removed to have molecular printing membranes in the film. It is expected to use these films with MIM to verify whether the sensor is selective for methylene blue.

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Solubility of NO from combustion gases in amines solutions

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Abstract

This work studies the absorption of nitric oxide (NO) in primary amine (AMP) and tertiary amine solutions (TEA, MDEA), which can be used as an alternative treatment to the two main technologies used nowadays to control NOx emissions in flue gas streams: selective catalytic reduction (SCR) and selective non-catalytic reduction (SCNR)[1]. To analyze NO solubility, each amine solution (40% w/w) was placed inside a reactor and before the experiment, the amine solution was degassed using liquid nitrogen and vacuum. After two repetitions, it was assumed that the amine was fully degassed. The reactor was preheated at 35°C using a temperature controller and once the temperature was stable, the solubility at different absorption pressures was evaluated (1, 3, 5, and 7 bar) by measuring the pressure decay inside the reactor using a manometer. Using the ideal gas law and the difference between the initial and the final pressure the amount of NO solubilized in the absorbent liquid was determined. The results for the amines evaluated are AMP: 3.6131×10^{-3} $\frac{mol}{atm*L}$, TEA: 3.31×10^{-3} $\frac{mol}{atm*L}$ and MDEA: 2.28×10^{-3} $\frac{mol}{atm*L}$. The results obtained are higher than the NO absorption in water[2] 1.90×10^{-3} $\frac{mol}{atm*L}$ but lower compared to CO_2 absorption in MDEA[3] 6.54 $\frac{mol}{atm*L}$. According to Fine, N. et al, for tertiary amines the absorption of NO is in form of nitrate and nitrite and for primary amines the reaction will form unstable nitrosamines which will ready deaminate into a carbonization and nitrogen gas. Because of the facility to create nitrosamines rather than nitrate and nitrite[4], the highest absorption was found by AMP. Further analysis will be performed to verify that the absorption in AMP is giving unstable nitrosamines or whether there is absorption as nitrate and nitrites. Other types of absorbent liquids will be tested to improve the NO solubility.

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